NITROGEN ON MARS: INSIGHTS FROM CURIOSITY. J. C. Stern[1], B. Sutter[2], W. A. Jackson[3], Rafael Navarro-González[4], Christopher P. McKay[5], Douglas W. Ming[6], P. Douglas Archer[2], D. P. Glavin[1], A. G. Fairen[7,8] and Paul R. Mahaffy[1]. [1]NASA GSFC, Code 699, Greenbelt, MD 20771, jennifer.c.stern@nasa.gov, [2]Jacobs, NASA Johnson Space Center, Houston, TX 77058, [3]Texas Tech University, Lubbock, TX 79409, [4]Universidad Nacional Autónoma de México, México, D.F. 04510, Mexico, [5]NASA Ames Research Center, Moffett Field, CA 94035, [6]NASA Johnson Space Center, Houston TX 77058, [7]Centro de Astrobiologia, Madrid, Spain, [8]Cornell University, Ithaca, NY 14853

Introduction: Recent detection of nitrate on Mars [1] indicates that nitrogen fixation processes occurred in early martian history. Data collected by the Sample Analysis at Mars (SAM) instrument on the Curiosity Rover can be integrated with Mars analog work in order to better understand the fixation and mobility of nitrogen on Mars, and thus its availability to putative biology. In particular, the relationship between nitrate and other soluble salts may help reveal the timing of nitrogen fixation and post-depositional behavior of nitrate on Mars. In addition, *in situ* measurements of nitrogen abundance and isotopic composition may be used to model atmospheric conditions on early Mars.

Methods: The data presented are from analyses of solid Martian drilled and scooped samples by the Sample Analysis at Mars (SAM) instrument suite on the Mars Science Laboratory (MSL) Curiosity Rover. SAM performs evolved gas analysis (EGA), in which a sieved (<150 μm) and portioned (~76 mm^3) sample is delivered into one of SAM's quartz-glass cups and is subsequently heated from Mars ambient temperature to ~870 ºC [2]. Gas evolved during pyrolysis is continuously monitored using the quadrupole mass spectrometer (QMS), and a portion of this gas can be sent to the hydrocarbon trap (Tenax®) for gas chromatograph – mass spectrometer (GC-MS) analysis. The SAM instrument and the quantification of nitrate and perchlorate has been described in detail elsewhere [3]. Briefly, nitrate and perchlorate are identified and quantified by their thermal decomposition products, NO and O_2, respectively.

Results: Nitrate abundance reported by SAM *in situ* measurements ranges from non-detection to 681 ± 304 mg/kg [1] in the samples examined to date. Recent evolved gas measurements from Oudam (OU) and Marimba (MB) in the Murray formation represent the only samples SAM has measured so far in which no volatile perchlorate decomposition products were detected. This has fundamental implications on the geochemical history of Mars, and may be the first definitive evidence that perchlorate formation has not been pervasive at all times and places, challenging previous implications of Curiosity's analysis [4]. Nitrate was similarly below detection limits at MB and present at low abundance at OU (85 ± 35 mg/kg). Samples from
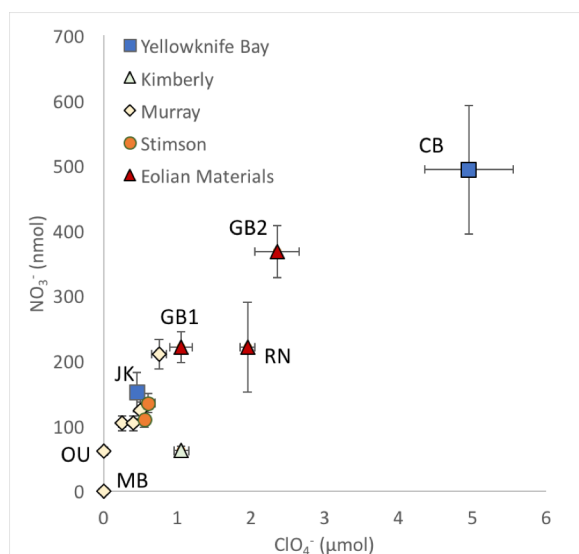

Figure 1. Nitrate vs. perchlorate abundance in samples measured by SAM to date.

the rest of the Murray and Stimson formations were relatively low in both nitrate and perchlorate when compared to eolian materials, with the exception of Buckskin (BK) in the Murray Formation.

Discussion: The linear correlation (Figure 1) between nitrate and perchlorate reflects the consistent nitrate/perchlorate (average $NO_3^-/ClO_4^- = 0.2 ± 0.1$) of the sampled materials. The similarity in NO_3^-/ClO_4^- among all sedimentary rock samples measured thus far from Gale suggests one of two scenarios: 1) Constant accumulation rates for nitrate and perchlorate, where differences in measured abundances represent differences in exposure time and/or local environmental enrichment, or 2) Variable deposition of nitrate and perchlorate over the millions of years of sedimentation of Gale Crater sediments, where post-depositional processes have averaged NO_3^-/ClO_4^- and abundances are dependent upon exposure to diagenetic fluids.

Constant accumulation: The lack of variation in NO_3^-/ClO_4^- is consistent with steady state processes of production and possibly loss of both species over the time of sediment deposition represented by the formations sampled by SAM/MSL at Gale Crater. Such steady state processes have been observed in the most hyper-arid places on Earth such as University Valley in

the McMurdo Dry Valley in Antarctica [5] where soil NO_3^-/ClO_4^- does not vary significantly with depth reflecting relatively unchanging perchlorate and nitrate depositional rates. Both sub-aerial sandstones in the Stimson and lacustrine mudstones in the Murray have relatively low concentrations of nitrate and perchlorate, perhaps representing steady state deposition of both species. While there is significant variation in the Murray materials, from fairly high nitrate abundance at BK (290 ± 120 mg/kg) to non-detection of nitrate at MB, this may be due to aqueous activity on a local scale. In this scenario, enrichment of nitrate and perchlorate at Cumberland (CB) is either due to longer exposure of these sediments or local concentration in this lacustrine environment. The absence of similar enrichment at John Klein (JK) could be attributed aqueous alteration via diagenetic flow through fractures [6], specifically, removal by sulfate (and boron) bearing fluids that formed $CaSO_4$ veins here.

The fact that perchlorate was not detected at either MB or OU has major implications for the detection of organics in these sediments. It is possible that the same post depositional fluid alteration processes that leached perchlorate salt from these samples also leached out soluble organics. At the same time, the lack of perchlorate salts in the samples would facilitate a greater recovery of any native organic molecules released from the samples by pyrolysis due to reduced thermal decomposition and transformation of organic compounds by combustion or chlorination that has been observed in other martian mudstone samples containing perchlorates [7].

Post-depositional Processing: The variation of nitrate and (per)chlorate abundance over at least 2 orders of magnitude may be a function of post depositional processes instead of surface exposure time. In this scenario, post-depositional impact, fluvial, eolian, aqueous, and/or other erosive processes could have acted to mix and redistribute similarly soluble perchlorate and nitrate resulting in the observed constant ratio.

Evidence for post-depositional fluid alteration over the Yellowknife Bay, Murray, and Stimson formations comes in the form of $CaSO_4$ veins which were recently associated with the detection of boron [8], another element that makes very soluble complexes. In this scenario, wetter conditions could have leached nitrate and perchlorate from stratigraphically higher formations such as the Stimson and the Murray to the lower Yellowknife Bay sediments.

The intermediate abundances of both nitrate and perchlorate in eolian materials Rocknest (RN), and Gobabeb 1 and 2 (GB1, GB2) (Figure 1) suggest physical mixing between two end-member sources. Eolian samples have NO_3^-/ClO_4^- similar to drilled sedimentary

samples, consistent with the notion that these materials are locally sourced. Although RN contains a small portion of global martian dust [9], it is otherwise thought to be locally sourced, and its ratio is consistent with the CB and JK samples from nearby Yellowknife Bay. GB1 and GB2 materials were taken from Bagnold dunes that are active today and likely locally sourced based on their larger particle size (>45-500 µm).

Timing of nitrate deposition: While little is known regarding the timescales over which nitrate and perchlorate deposition occurred, comparisons of NO_3^-/ClO_4^- measured in rocks of various ages and in global martian dust could provide a better understanding of when these processes were active, and if they are still active today. Although production of NO in the ionosphere has been reported [10,11], there is no evidence for current dry deposition of nitrate. Therefore, it is possible that all nitrate on Mars is relic, with no modern contribution. This is supported by strong evidence that impact processes may account for the observed nitrate abundances [12]. Therefore, it is likely that all nitrate was formed and deposited prior to or during the emplacement of Gale Crater sediments, and what we see is a mixing of nitrate transported into Gale Crater from elsewhere with an *in situ* component.

The nitrogen isotopic composition ($\delta^{15}N$) of nitrate from an unconsolidated surface sample with a significant component of martian dust may shed light on the timing of nitrogen fixation, as this value would be skewed towards atmospheric N_2 ($\delta^{15}N \approx 574\text{‰}$[13]) if there is a modern mechanism for nitrogen fixation. $\delta^{15}N$ measured in ancient Hesperian rocks at Gale Crater should reflect the $\delta^{15}N$ of atmospheric N_2 during nitrate deposition and formation, could also be used to constrain atmospheric loss of N_2 and the atmospheric pressure at the time of deposition. Therefore, these measurements will a priority for future SAM investigations.

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